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13. ABSTRACT *(Maximum 200 words)*

During the past year strategies were developed to synthesize ET monomers containing one functionalized side chain (for pendant attachment) and two functionalized side chains (for main chain copolymer incorporation). The redox behavior of these ET monomers and polymers is identical to ET itself.

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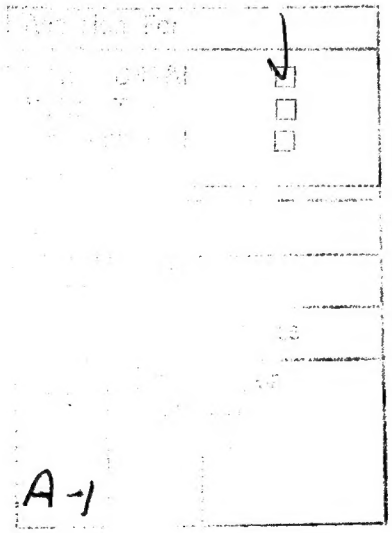
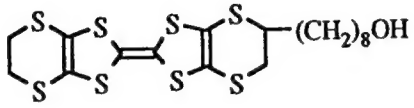


Introduction

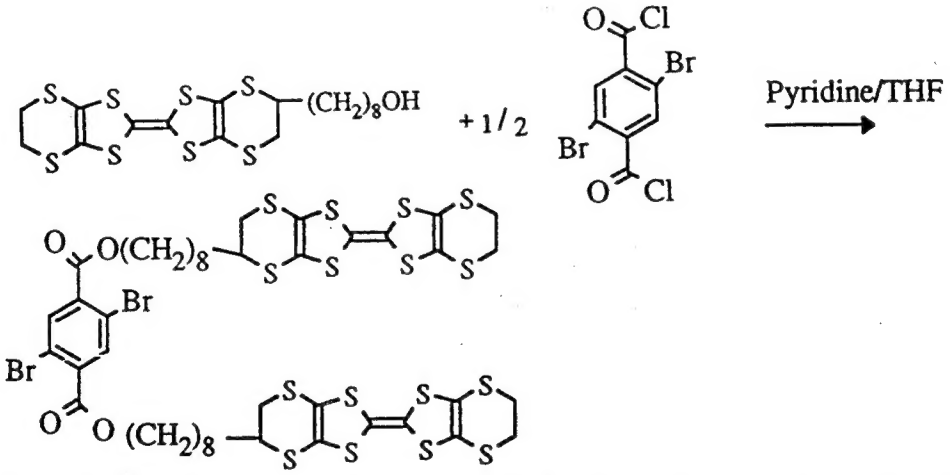
This report details the work accomplished in year 2 towards the design and synthesis of the first organic polymeric superconductor. During year 1 we established synthetic protocols for the preparation of TTF and ET monomers capable of incorporation as pendant groups on rigid-rod polymeric backbones. This year we have expanded this concept to include ET incorporation as a formal repeat unit in main chain copolymers.

Synthesis of Main-Chain Copolymers Incorporating ET Subunits

During this year we focused on the synthesis of ET monomers. The first such monomer was synthesized with a -(CH2)-$_8$OH side chain for attachment to a poly [p-phenylene] or poly[paraphenylene vinylene] backbone as a pendant group.



This monomer will be attached to a polymer precursor as follows:



A model compound with H in place of the two Br functionalities was prepared and its redox behavior studied to determine if the ET subunits behaved in a similar fashion to ET itself.

Three main chain copolymers were synthesized and their redox behavior studied in a similar fashion to the above model compound. The rationale for choosing to synthesize these polymers in addition to the previously discussed pendant polymers is outlined in our paper entitled (attached):

"Studies Toward the Design and Synthesis of Superconducting Organic Polymers: Main Chain Incorporation of ET Subunits"

This paper outlines both the synthesis of the difunctional monomer, the polymer synthesis and their cyclic voltammogram behavior. They compare quite well with ET itself, so we are currently proceeding to form charge transfer complexes with these polymers for low temperature conductivity studies. This paper will be presented at the Spring National Meeting of the American Chemical Society in Anaheim, CA. in April.

Personnel

The following postdoctoral students worked on this project during the year:

Dr. Tom Hall
Dr. LinFang Zhu

two graduate students worked part-time on the project:

Mr. Mingqian He
Mr. John Thurmond

two undergraduate research assistants worked part-time on the project:

Mr. Hu Li
Mr. William Veldhuyzen

Dr. Hall and Dr. Zhu have since accepted permanent positions in industry, and replacements are currently being recruited to continue the polymer synthetic work.

STUDIES TOWARD THE DESIGN AND SYNTHESIS OF SUPERCONDUCTING ORGANIC POLYMERS: MAIN CHAIN INCORPORATION OF ET SUBUNITS

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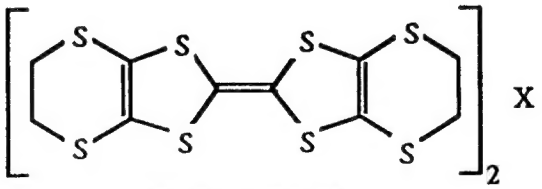
Introduction

During the past twenty years there has been an explosion of interest in conducting organic materials. This interest has encompassed a variety of new material classifications from the first organic metal TTF-TCNQ (1973) and similar charge transfer salts,[1] to an ever increasing family of conducting polymers such as polyacetylene, poly(p-phenylene), polythiophene and poly(p-phenylene vinylene), where conductivities as high as 10^5 S/cm have been achieved.[2] During this time there has also been a continuous interest in organic superconductors, however the relatively low temperatures that must be achieved in order to observe superconductivity has been a deterrent to their development. In addition, organic superconductors are normally produced as electrocrystallized salt crystals, which are quite small and fragile, thus severely limiting their practical application. In this study we will outline an approach to the design of the first organic polymeric superconductors.

Problems Inherent in the Design of Polymeric Organic Superconductors

A large percentage of known organic superconductors has focused on electrocrystallized salts such as $(BEDT\text{-}TTF)_2X$, where X represents a large family of counter anions.[3] Exhaustive studies of this system from 1986 to the



$(BEDT-TTF)_2X$
$(ET)_2X$

present has greatly enhanced the understanding of the effect of crystal packing of both ET and X moieties upon T_c and has resulted in higher temperature organic superconductors.[4] Even a cursory reading of the voluminous literature on $(ET)_2X$ superconducting salts reveals that structure-property

relationships are both extremely important to the design of high T_c organics, and extremely difficult to generalize. One of the problems in electrocrystallization is that it is not possible to rationally control the nanostructure of the materials formed. Our approach to superconducting polymer design is twofold: (1) by using rigid polymer backbones as templates for TTF or ET donor group assembly in intermolecular ensembles, and (2) incorporating ET moieties as formal main chain copolymer repeat units alternating with flexible spacers which will allow potential main-chain intermolecular π-stacking. In this paper we will discuss how the latter approach is being implemented in our program. This is illustrated in Figure 1.

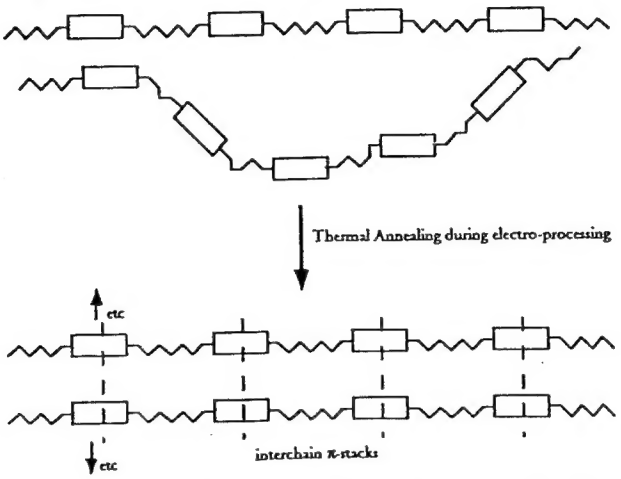
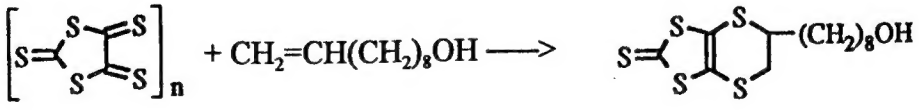


Figure 1. Model Structure for Assembly of Potentially Superconducting Main-Chain Polymers.

Synthesis of ET Monomers

Our initial goal was to synthesize ET monomers that could be incorporated in various main-chain polymers as a formal repeat unit. ET moieties were synthesized which incorporated alkanol side chains of varying length. This approach is outlined in Scheme 1 for an 8-carbon spacer:



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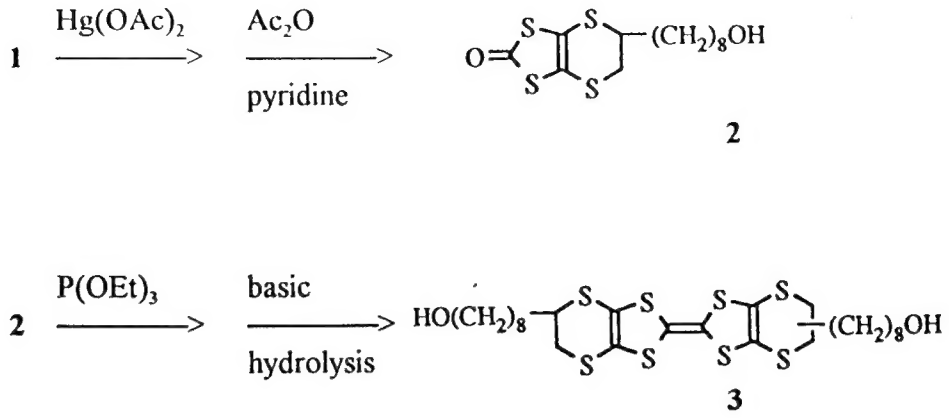
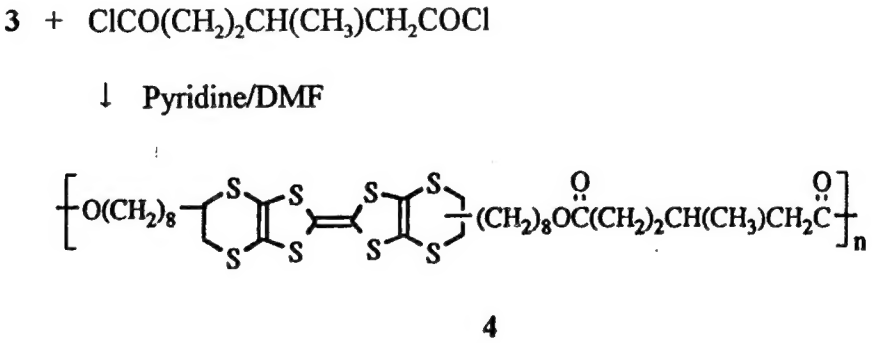


Scheme 1. Typical Synthesis of ET Copolymer Precursor.

The disubstituted ET is a mixture of positional isomers, which were converted to copolymers without separation. In fact, the incorporation of the two positional isomers in the copolymer chain may be an advantage in terms of solubility and subsequent processing.

Copolymer Formation

Three copolymers were synthesized from monomer **3**: two polyesters by condensation with either 3-methyladipoyl dichloride or terephthaloyl dichloride, and a polyurethane by condensation with 1,6-diisocyanatohexane. The formation of these polymers is illustrated in Scheme **2**.



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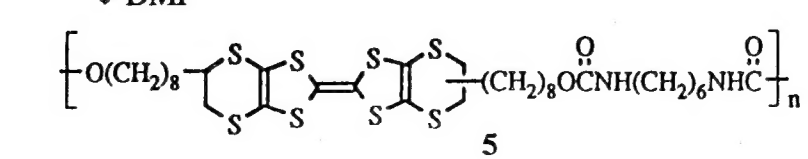

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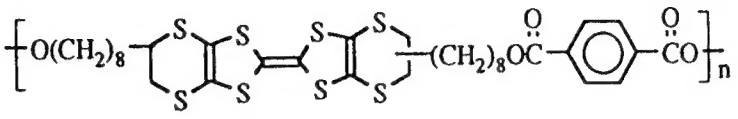
3 + $ClCOC_6H_4COCl$

↓ Pyridine/THF



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Scheme **2**. Synthesis of Copolymers Incorporating ET Moieties as Repeat Units.

The three copolymers were obtained in good yield and were fully characterized by FT-IR, FT-NMR, and UV spectra, DSC, GPC, and C, H, N analysis. The copolymers were soluble in common organic solvents such as THF and chloroform, and stable, transparent free-standing films could be cast from static solution. Complete details of both the synthesis and characterization of these polymers will be published in the near future.[5]

Oxidative Behavior of Copolymers

The redox behavior of the three copolymers was studied *via* cyclic voltammetry as 1 mM solutions in CH_2Cl_2 containing 0.1 M tetrabutylammonium perchlorate at a scan rate of 100 mV/sec at room temperature. The redox behavior of the incorporated ET moieties is critical to future conductivity studies in that the radical cations must be formed prior to self assembly *via* intermolecular π-stacking. The CV of the three polymers are shown in Figure 2.

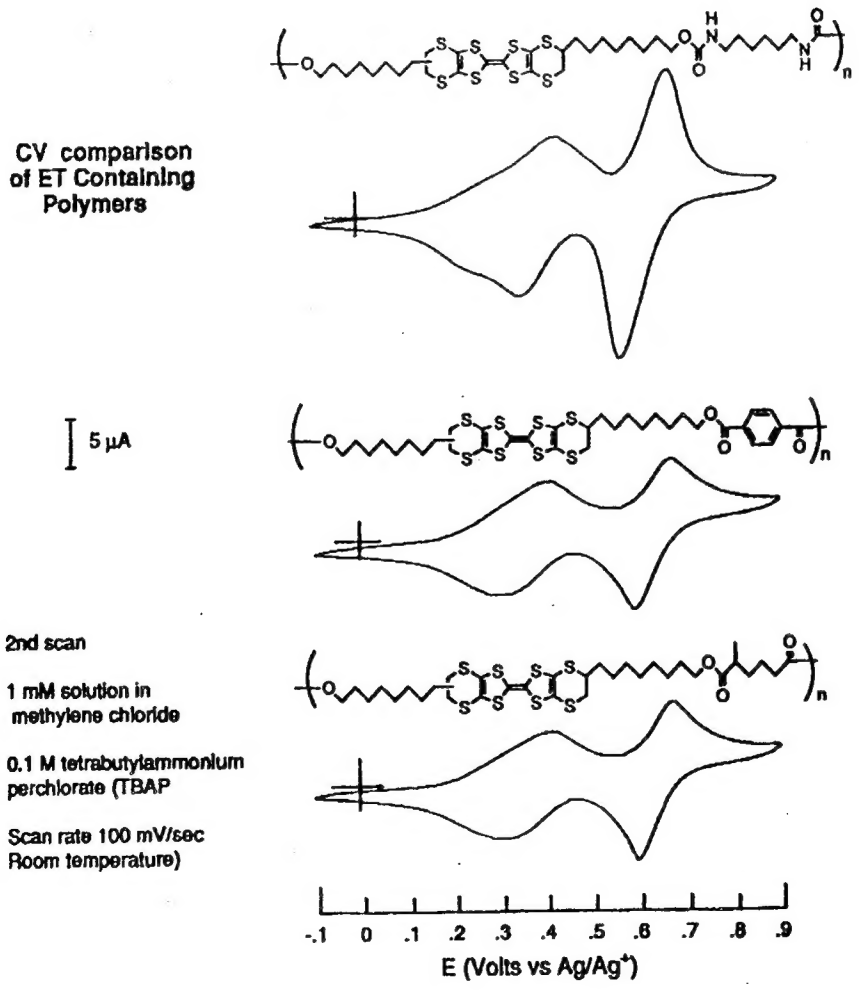

Figure 2. CV Comparison of ET-Containing Polymers.

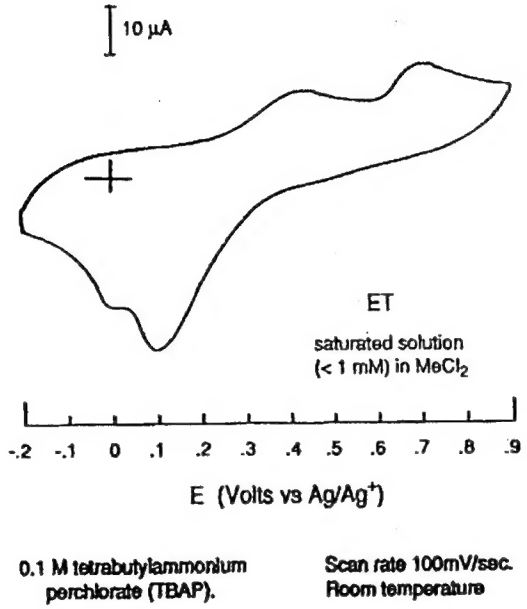

Figure 3. Cyclic Voltammogram of ET.

The redox behavior is quite similar to ET, illustrated in Figure 3. Thus, it appears that stable charge states are attainable in these polymers and the next stage, casting oxidized films for low temperature conductivity studies, can be accomplished. These studies are currently underway, and will be discussed in detail in a future report.

Conclusions

Stable processible polymers in which ET is incorporated as a formal repeat unit have been synthesized. These copolymers show redox behavior in solution which exactly parallels free ET under similar experimental conditions. Self assembly under thermal annealing conditions is currently underway to

determine the amount of π-stacking of the oxidized ET segments that can be achieved prior to low temperature conductivity studies.

Acknowledgements

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2. For examples, see "Handbook of Conducting Polymers," Vol. 1 and 2, T. Skothem, ed., Marcel Dekker, New York, 1986.

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